DRAFT VERSION

Dry-etching Continuous Surface Profiles Into Infrared Semiconductor Materials

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Randall L. Lindsey
Principal Investigator

SY Technology, Inc.
654 Discovery Drive
Huntsville, AL 35806
(256)922-9095

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SY Technology, Inc.

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1. Introduction

Etching high-efficiency diffractive optical elements (DOEs) into InSb substrates, using multiple binary masks, has proven to be problematic. This microfabrication method (sometimes called binary optics technology) is time-consuming, costly, and sensitive to alignment errors. Other major problems unique to InSb and the multi-mask process, are polymer buildup and substrate fracturing as a result of stresses experienced in subsequent etch levels. Since these do not appear to be problems with a single etch process, a new process is needed which achieves fabrication of high-efficiency DOEs with only a single mask and a single etch step. This effort investigates the application of gray scale mask technology to etching high-efficiency DOEs and micro-optical elements in InSb and InAs.

1.1 Diffractive Optic Design and Fabrication Process

Kinoforms are diffractive optical elements (DOEs) which modulate the phase of incident light using a modulo-2π grating surface relief structure. The surface profile of each kinoform grating zone is smooth and continuous, except at the zone boundaries where 2π phase discontinuities occur. Diffractive optics are optical elements that use the principle of diffraction to produce light redistribution, as opposed to conventional optics that use the principle of refraction. Figure 1 shows the physical difference between a conventional simple lens and a diffractive lens. The refractive lens profile is converted to a diffractive profile by removing multiples of 1 optical wavelength so that the maximum height or thickness of any feature is one wavelength deep on the surface across the lens diameter. Figure 1a shows the unfractured refractive element, and Figure 1b shows the ideal analog diffractive surface relief profile. Figures 1c, 1d, and 1e depict digital approximations of the ideal analog profile shown in Figure 1b. Figure 1c shows a binary, or half wavelength, lens made from a single chrome mask. Figures 1d and 1e show multilevel approximations of the analog profile, with Figure 1d showing 4 steps made from 2 masks, and Figure 1e showing eight steps made from 3 masks. If you follow the progression, it continues as a function of $2^{(\#\text{ of masks})}$.

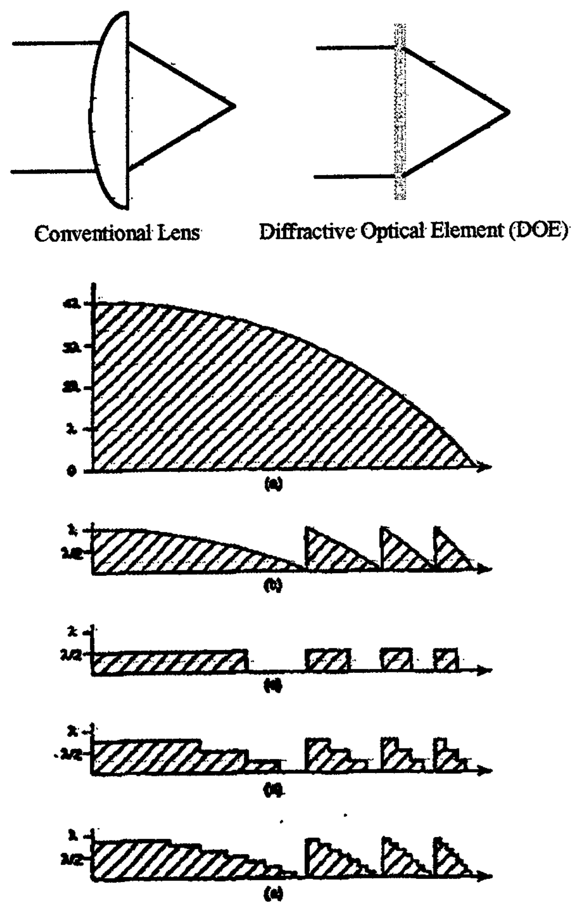

Figure 1. Diffractive design process.

Until recently all masks used in the fabrication of diffractive optics were binary, meaning that the chrome on glass masks have either opaque or transparent regions. This is illustrated in Figure 2. This binary mask pattern is transferred into photoresist via contact lithography. A glass substrate is prepared by spin coating a thin layer of photoresist. The photoresist is soft baked to remove any residual solvents. The mask is precisely placed in contact with the photoresist coated substrate using a mask aligner. The substrate is exposed to high intensity ultraviolet light. The areas of photoresist covered by the chrome receive no UV and do not expose. The exposed photoresist is then removed during the development process. Through this process, the mask pattern is transferred into the photoresist. This process step is followed by etching whereby substrate areas not covered by resist are etched away. Areas of the substrate protected by the resist are not etched. In this way, the original mask pattern creates a binary relief pattern in the substrate. Multiple masks together with multiple spin-coat and etch steps can be used to create complex stair step relief patterns in the substrate. In this way, a continuous lens profile can be approximated by a stair step like structure. The most demanding step in this process is to accurately align the subsequent mask layers with the first mask layer. This alignment process is both time consuming and expensive.

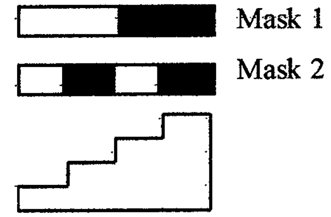

Figure 2. Binary Mask Approach.

The theoretical diffraction efficiency (the amount of light diffracted into the desired order) of a kinoform is 100%. Binary Optical Elements (BOEs) are a special class of diffractive elements that approximate the ideal kinoform zones using stair-stepped relief structures. The more steps used per zone, the closer the approximation is to the ideal kinoform and the better the diffraction efficiency. The stair steps are fabricated using multiple binary chrome masks in a photolithographic process previously described. The etching process uses either reactive ion etching (RIE) or ion milling.

Table 1. Comparison of diffraction efficiency for multi-level phase structures and gray scale continuous structures.

Process	Number of Masks	Number of Phase Levels Per Zone	Theoretical Diffraction Efficiency
Binary	1	2	40.5%
Binary	2	4	81.0%
Binary	3	8	94.5%
Binary	4	16	98.7%
Binary	5	32	99.8%
Gray Scale	1	continuous	100%

Standard multi-level diffractive optical elements are generally fabricated using no more than about four masks. As shown in Table 1, the more phase levels, the higher the theoretical diffraction efficiency. (Tabulated diffraction efficiency assumes no mask alignment error and no etch depth error.) Yet with more levels comes the burden of multiple alignments and smaller minimum feature sizes which are harder to align. This multi-step process is time consuming, costly, and highly alignment sensitive. Even with a perfect alignment of each mask level, the final result is only a stair-stepped approximation of the ideal kinoform surface profile. Figure 3 illustrates this using a gray scale mask in place of the two binary masks required for a 4-level device. Since no alignment is necessary, the result is the binary approximation of the ideal continuous surface profile.

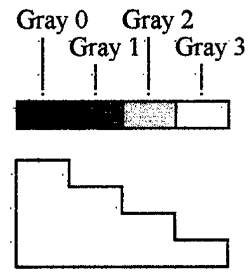

Figure 3. Gray scale mask of the binary approach.

The continuous gray scale mask fabrication technique offers the potential of fabricating the ideal kinoform diffractive surface profile (100% diffraction efficiency) with only a single mask. Figure 4 illustrates this. A single mask eliminates the multiple alignment steps that are necessary with the binary process. The reduced time and effort required for this process results in lower fabrication costs. In addition to decreased errors due to alignment, the continuous surface profiles are theoretically 100% diffraction efficient, as shown in Table 1 above.

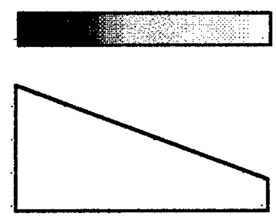

Figure 4. Continuous gray scale mask approach.

1.2 Identification of the Problem

The primary problem with gray scale masks is the initial process development. Unlike the binary process, the gray scale optical densities, photoresist exposure and development times, etch rate selectivity, and etch time must be precisely calibrated for each new job. With the binary process, only certain points on the zone are etched at any one time. All other points are protected with photoresist. When the correct etch depth is achieved for those particular points, the process is repeated by etching the previously unetched points and protecting the previously etched points. The gray scale process requires that all points on the zone be etched simultaneously. The desired height variation on the zone profile is achieved by precisely controlling the etch rate at every point on the zone. To achieve this generally requires considerable initial experimentation. However, once the process is calibrated and stable, the cost benefits can be realized.

Although gray scale mask technology has been used to etch many different materials[1], certain infrared semiconductor materials, such as InP, InSb, and InAs, have not yet benefited from

[1] SY Technology, Inc. has RIE etched fused silica, silicon, and germanium, and ion milled stainless steel and nickel using gray scale masks.

the gray scale microfabrication process. Dry etching of compound semiconductors[2] using binary masks to produce microcircuits is a technology area that has matured over the past five years. However, processes for etching high efficiency diffractive and micro-optical elements into these semiconductor materials (e.g., InSb, InAs) has not been adequately developed. This was why this Phase I SBIR was proposed.

The two major problems associated with etching InSb - polymer buildup and substrate fracturing - should be eliminated using a the gray scale mask approach. The gray scale mask eliminates the need for a multi-mask process; the single etch process eliminates the polymer buildup and substrate fracturing problems. In addition to eliminating these problems, there are several realized advantages of using gray scale masks:

1. No alignment errors.
2. Ability to produce continuous surface profiles.
3. Produces optimal diffraction efficiency.
4. One step exposure (a single mask) reduces labor cost and laboratory expense cost.

[2] S.J. Pearton, U.K. Chakrabarti, A. Katz, A.P. Perley, and W.S. Hobson, "Comparison of $CH_4/H_2/Ar$ reactive ion etching and electron cyclotron resonance plasma etching of In-based III-V alloys", J. Vac. Sci. Technology B 9 (3), May/Jun 1991.

2. Results of Phase I Work

2.1 Phase I Goal

The main goal of the Phase I research was to determine the feasibility of fabricating high efficiency diffractive and refractive elements in InSb and InAs substrates using a new gray scale mask technology. This goal was achieved! High-efficiency, continuous surface profiles were successfully etched into InSb, InAs, Ge, GaP, TiO_2, $SrTiO_3$, and YSZ. In addition, prototype off-axis continuous profile field grating lenses, fabricated in InSb, will be delivered to the US Army Night Vision and Electronic Sensors Directorate upon the completion of the Phase I contract. The prototype lenses will be used by NVL in fielded night vision equipment for testing and evaluation.

This proves not only the feasibility of fabricating continuous surface profiles into IR materials, but also demonstrates SY Technology's ability to successfully manufacture high-efficiency diffractive/refractive optics in IR materials for wavebands ranging through the near-IR, mid-IR, and far-IR. It also demonstrates SY Technology's commitment to meeting and exceeding our customer's expectations, and SY Technology's ability to bring leading-edge technology items into commercialized applications.

2.2 Phase I Technical Objectives

2.2.1 1st Technical Objective - Etch Chemistry Development

The first technical objective was to determine and develop etch chemistries for using methane-hydrogen-argon (MHA) reactive ion etching (RIE) to pattern continuous structures into InSb and InAs. Our results determined that polymer build-up during etching prohibited the controllable transfer of the continuous mask pattern (photoresist) into the target material (InSb). Three dry etching RIE chemistries (fluorine, chlorine, and hydrogen based) were tested during Phase I. None of these RIE chemistries were found feasible for controllable transfer of the continuous profile patterns into the IR substrates. The noted exceptions, of course, are Si and Ge. SY Technology, Inc. has already demonstrated the ability to etch continuous profile surfaces into these materials using conventional fluorine-based RIE chemistries. Figure 5 shows a smooth, continuous profile lens fabricated in Ge using gray scale mask technology. These lenses were part of a commercial beam expander made for a MEMS Optical, Inc. customer.

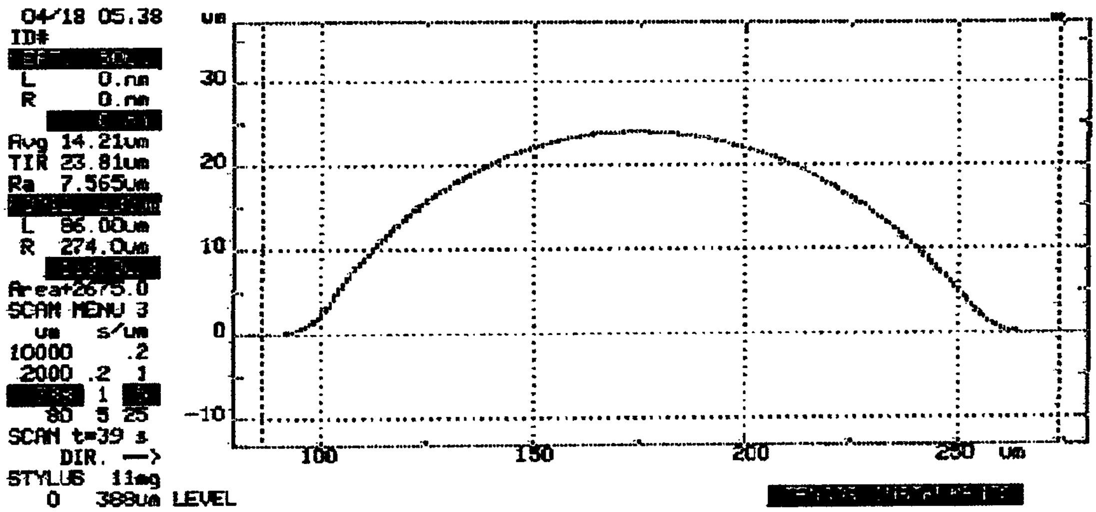

Figure 5. A profilometer scan of a smooth, continuous profile lens fabricated in Ge by SY Technology, Inc. using gray scale mask technology.

2.2.1.1 Fluorine-based Etch Tests

We tried etching GaP, TiO_2, $SrTiO_3$, YSZ, diamond, substrates in both SF_6 and CHF_3 gases without success. We were able to obtain very slow etch rates (~35 angstroms per minute) for GaP and TiO_2, but no measurable etch results for the other materials. As an aid in determining the optimal etch gas ratios needed for proper etching of these materials, we used a software package called CARD DOE and CARD AOD (Computer Aided Research and Development Design of Experiment, and Analysis of Data). By using the CARD software, we were able to statistically determine the optimal gas flows and power levels needed to optimize surface roughness on our etched materials. This was made possible by analyzing the results obtained through statistical experiment design. The information derived from this type of experimental analysis not only saves enormous amounts of time in sample preparation and runs, but greatly reduces the experimental error associated with a given process. Therefore, the level of confidence in the final analysis can be significantly improved when compared to traditional experimental design processes.

2.2.1.2 Chlorine-based Etch Tests

In the absence of an available Chlorine etcher, we asked Coherent, Inc. in Auburn CA to perform an etch test of GaP using their chlorine and boron-trichloride reactive ion etcher. As you recall, GaP is an excellent near-IR transmissive material for wavelengths 0.55 μm to 2.0 μm. Coherent agreed to characterize this etch at no charge. By the last week of February, Coherent successfully etched GaP using their boron-trichloride (BCl_3) chemistry, obtaining an etch rate of about 1400 angstroms/minute.

However, after discussions with Byong Ahn, the NVL Phase I COTR, we stopped pursuing etch tests on the various high index materials until the work on the InSb and InAs materials were completed. Due to time/funds constraints, no more work was performed during this contract on etch characterization of the high index optical materials.

2.2.1.3 MHA Etch Tests

On 18 Feb 98, the etch chamber modifications on the MICOM reactive ion etcher were completed sufficiently to begin chemistry validation experiments. The chemistry flow rate starting points for the experiments were derived from previous data taken from earlier etch tests. Five different samples were etched for 15 minutes each. The following settings were used: 4 sccm methane, 20 sccm hydrogen, 10 sccm argon, 75 mTorr pressure, 50 watts power. The averaged, compiled measurements revealed an etch depth of 9051 angstroms. This yields an etch rate of 603 angstroms per minute. This value agreed with predicted estimates of etch rates between 400 and 700 angstroms per minute. Therefore, we assumed that the modifications to the etch chamber, and the flow rates we selected to date accurately reproduce previous results obtained in other MHA chambers. Figure 6 shows a micrograph of the InSb substrate following the 15 minute etch in a MHA chamber.

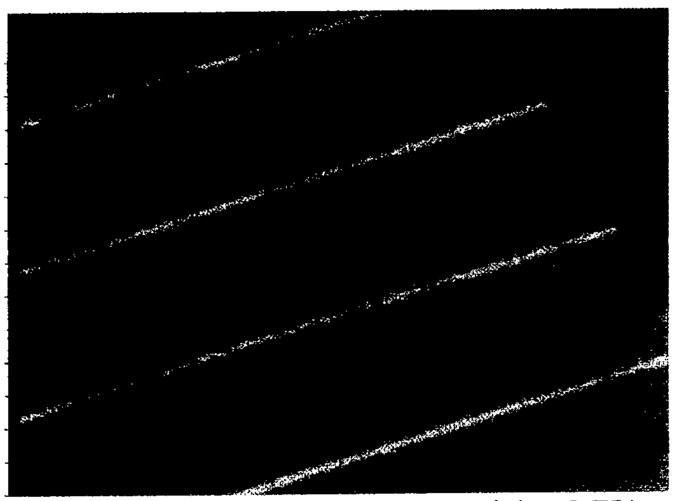

Figure 6. InSb sample after a 15 minute etch in a MHA reactive ion etcher. The etch rate was 603 angstroms per minute.

As was expected with the MHA process, a polymer build-up began on the surface of the photoresist during etching. One of the goals of this effort was to try to overcome the deposition of the polymer enough so that the photoresist could be removed at a selective rate to the base material. The ideal selectivity would be in the range of 0.5:1 to 20:1, with the etch rate of the base material compared to the etch rate of the photoresist (ER_{base}:ER_{PR}).

The rate of polymer formation in a continuous MHA plasma can be controlled by the introduction of oxygen to the process. A small amount of oxygen (~1%) can drastically reduce the rate of polymer growth. Therefore, by controlling the amount of oxygen introduced into the plasma during a MHA etch, we hoped to control the polymer buildup on the surface of the photoresist without drastically affecting the selectivity of the desired etching materials. We found though that simply adding oxygen also affects the etch rate of the base material. The increase of oxygen basically starved the plasma of reactants.

In our tests, the InSb samples were etched with varying concentrations of oxygen, ranging from zero to 2.0 sccm flow rate. Even with an optimal oxygen flow rate, one where the polymer formation was a minimum, the polymer formation on the surface of the photoresist made controllable selectivity virtually impossible. Therefore, it appeared that without substantially more research and funding, the use of MHA reactive ion etching to transfer continuous profile surfaces into InSb was not feasible. It was at this point that we decided to pursue dry etching the grayscale profiles into the InSb using ion milling.

2.2.1.4 Ion Mill Etch Tests

Even though the RIE chemistries we investigated did not deliver our expected results, the ion milling approach did prove capable. The ion mill approach has been proven to etch a wide variety of materials unetchable in traditional reactive ion etchers. SY Technology, Inc. has previously demonstrated this approach in fabricating field grating lenses for the U.S. Army Night Vision Directorate through a contract with Telic Optics[3]. We have also recently demonstrated the ability to successfully transfer continuous profiles into calcite, through a contract with MEMS Optical. Because of these successes, we felt confident that we could successfully use the ion mill to etch continuous surface profiles into our infrared semiconductor samples. This assumption was correct. <u>We have successfully etched continuous surface profiles into both InAs and InSb using the ion mill</u>. Section 2.3.2 details this success with micrographs and profilometer scans of a continuous surface profile off-axis field grating lens etched into InAs and InSb.

2.2.2 2nd Technical Objective - Photoresist Exposure Development

The second technical objective was to determine and develop a precise photoresist exposure and development process to accurately replicate gray scale mask features. The photoresist which showed the most promise was Shipley STR 1000 series photoresists. We were able to develop a process to successfully transfer the gray scale mask pattern into the photoresist, a crucial link in successfully making continuous surface profiles in various materials.

2.2.2.1 Lithography Simulation Results

The photoresist exposure process development was modeled using Prolith lithographic simulation software, by Finle Technologies. The simulation results were used to approximate starting points for the various process parameters used: exposure, development, and bake times, photoresist depth, gray scale optical densities, photoresist characteristics, and exposure dose. The simulation provided some very useful information about the expected photoresist profiles. Figure 7 and Figure 8 illustrates some of the Prolith simulation results.

[3] Telic Optics Purchase Order 960828B: Multi-level diffractive lens etched in InSb.

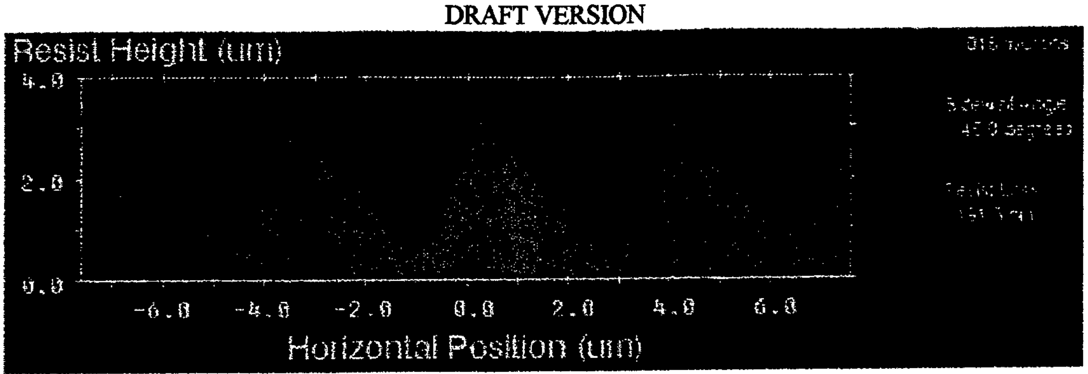

Figure 7. Prolith simulation showing the expected photoresist profile following development.

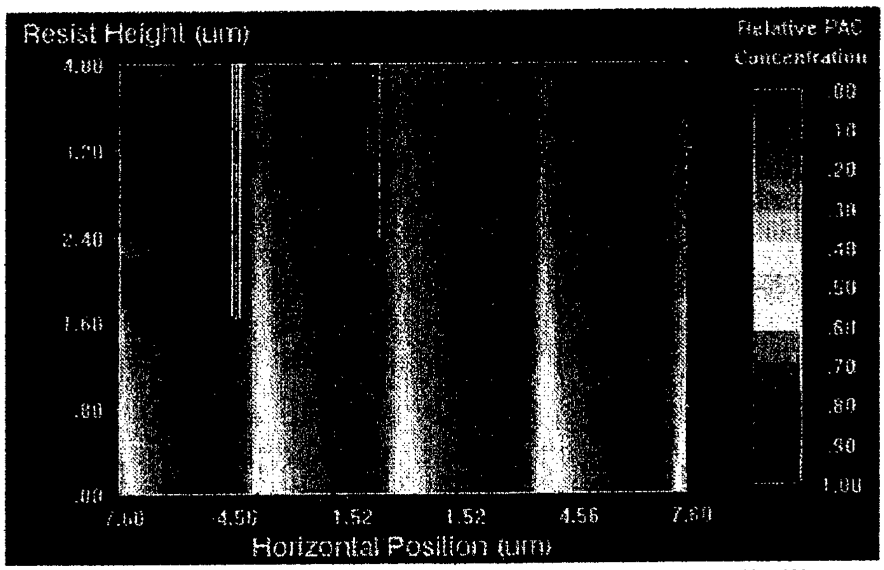

Figure 8. Aerial image of the photomask. This picture graphically illustrates the relative concentration of the photo-active compound, which is the variation of exposure within the photoresist layer.

The following list shows the parameters used in this simulation:

Wavelength:	365 nm
Illumination:	Mercury lamp (I-line)
N.A.:	0.40
Reduction:	10X
Partial Cohr:	0.46

Resist parameters:

A:	0.50 (1/μm)
B:	0.067 (1/μm)
C:	0.0242 (cm^2/mJ)
n:	1.63 (index of refraction)

Resist thickness: 4.0 μm
Pre-bake: 100°C, hotplate, 60.0 sec.

Exposure dose: 1750.0 (mJ/cm^2)
Develop time: 30.0 sec.

The use of Prolith has enabled rapid experimentation to determine the limitation and trends of the lithographic process. The modeling effort allowed us to determine the proper gray scale range and the linear portion of the photoresist response function. This is a direct result of the near perfect linear blazed zone in the photoresist shown in Figure 11.

2.2.2.2 Grayscale Pattern Calibration and Photoresist Selection

In order to properly calibrate the removal of photoresist, a stepped grayscale array reticle must be made and used to pattern the photoresist. Once patterned with this stepped reticle, the amount of photoresist removed as a function of dose must be measured. The data collected in this manner is used to create a calibration curve which compares the amount of photoresist remaining after the corresponding dose. The calibration curve represents the exposure characteristics of the specific photoresist used and the thickness of the photoresist before exposure. Therefore, after a specific photoresist has been calibrated, any change in process variables (photoresist, photoresist thickness, developer, bake time, or other particular process parameters) would require a complete recalibration of the grayscale values.

The following table (Table 2) contains a list of photoresists we used in determining the best photoresist to use for processing grayscale patterns. The key characteristic we looked for was the linearity of the grayscale range for calibration purposes.

Table 2. Photoresist List.

Manufacturer	Photoresist	PR Thickness	Resist Type	Results
Shipley	S-1805	0.2-0.7 μm	positive	marginal
OCG	OCG-897I	0.5-1 μm	positive	good
Shipley	S-5209	0.5-1.3 μm	negative	marginal
Shipley	S-3813	0.5-2 μm	positive	great
Shipley	STR-1045	2-10 μm	positive	excellent
Shipley	STR-1075	5-18 μm	positive	excellent
Hoestz	AZ-4903	10-20 μm	positive	good
Shipley	STR-1110	10-30 μm	positive	excellent
Microchem	SU-8	20-80 μm	negative	good

Based on these preliminary results, we concluded that the Shipley STR-1000 series of positive photoresists were the best ones to use for this research effort.

2.2.3 3rd Technical Objective - High Index Material Etching

The third technical objective originally was to determine the feasibility of fabricating a gray scale mask using thin film metal oxide coatings. At the kick-off meeting in December 1997, this objective was changed to pursue dry etching processes for various high index materials in the near-IR and mid-IR regions. Several candidate materials were selected and continuous surface profiles were successfully etched into them using the ion mill. High-efficiency, continuous surface profiles were successfully etched into InAs, Ge, Si, TiO_2, $SrTiO_3$, and YSZ. Section 2.2.1 documents the etch tests performed on these high index materials.

Toward the end of this contract, we were directed to stop work on characterizing the etch rates of these materials in order to pursue delivering an etched part in InSb of the off-axis field grating lens.

2.3 Extra Effort - Off-axis Field Grating Lens

During this reporting period, we were able to design an off-axis field grating lens from data previously received from the U.S. Army Night Vision Directorate through an old contract with Telic Optics[4]. A gray scale mask was also designed and fabricated. Using the lens data prescription, a simulation was performed to model the photoresist profile and approximate the process parameters.

The photoresist exposure process development was modeled using Prolith lithographic simulation software, by Finle Technologies. The simulation results were used to approximate starting points for the various process parameters used: exposure, development, and bake times, photoresist depth, gray scale optical densities, photoresist characteristics, and exposure dose. The simulation provided some very useful information about the expected photoresist profiles. Figure 9 illustrates a summary of the Prolith simulation results for the off-axis lens.

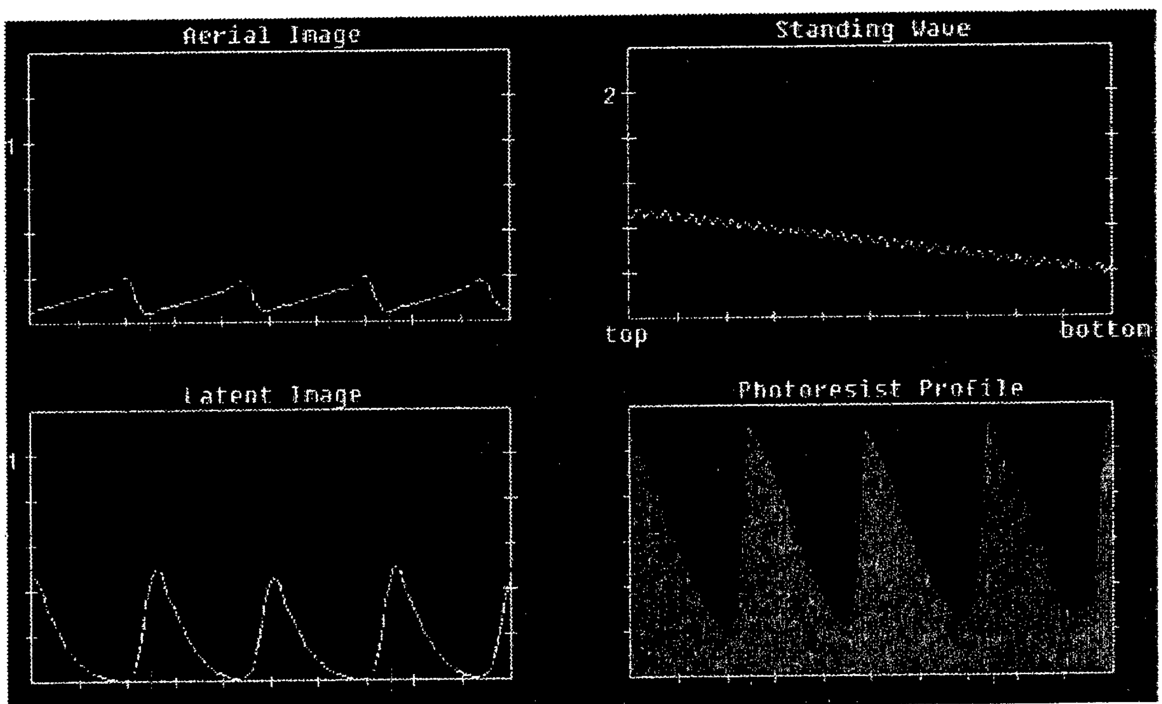

Figure 9. Prolith simulation results showing the projected aerial image, the standing wave pattern, the latent image following exposure, and the photoresist profile following development. This simulation was for the off-axis grating field lens design.

[4] Telic Optics Purchase Order 960828B: Multi-level diffractive lens etched in InSb.

2.3.1 Lithography Results

Using the gray scale mask for the off-axis field grating lens, we transferred the continuous profile field grating lens into photoresist on InAs, and InSb. The results are shown below in Figure 10 for InAs and Figure 11 for InSb. Note the excellent linearity of the blazes and the continuous profiles.

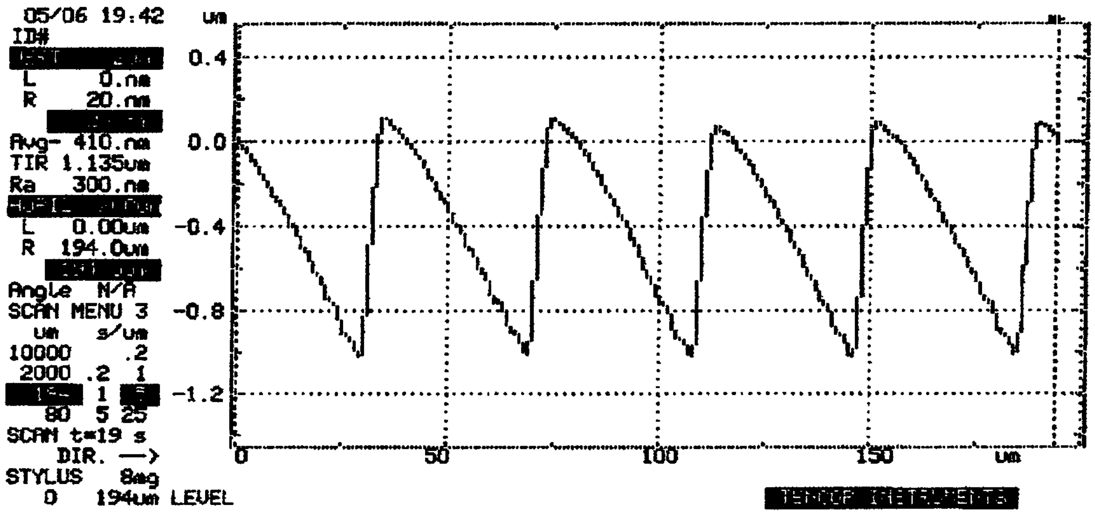

Figure 10. Continuous surface profile of the off-axis field grating lens patterned in photoresist on an InAs substrate.

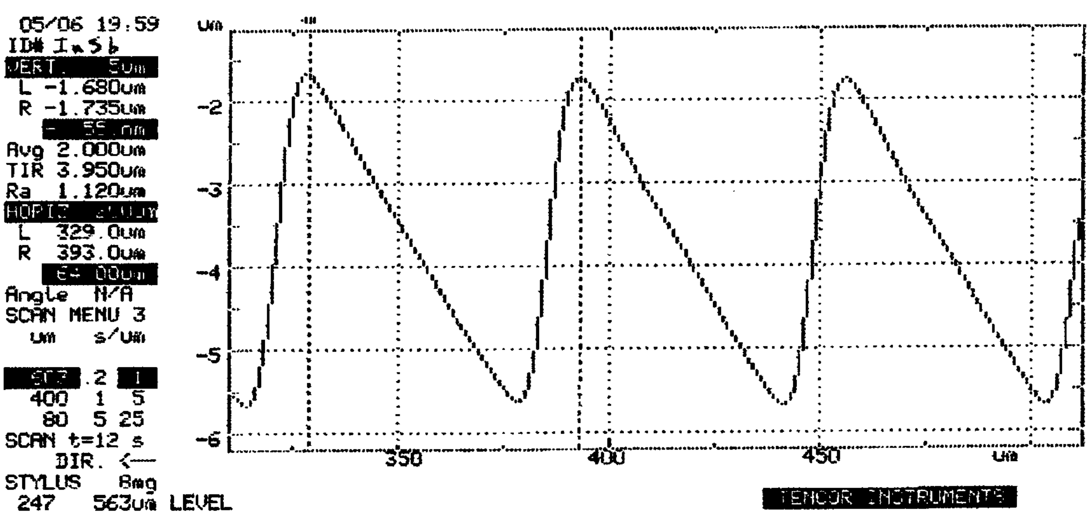

Figure 11. Continuous surface profile of the off-axis field grating lens patterned in photoresist on an InSb substrate.

2.3.2 Ion Mill Etch Results

Although the RIE chemistries we investigated did not deliver the results we expected, we did obtain excellent results from the ion mill approach. We successfully, and controllably transferred several continuous profile lens functions into InAs and InSb. Figure 12 illustrates this, showing a continuous surface profile off-axis field grating lens etched into InAs. Shown in Figure 13 is the profile measurement of the InAs field grating lens displayed in Figure 12. Figure 14 and Figure 15 are off-axis field grating lens profiles in InSb. The surface function, patterned in photoresist, was transferred into the InAs/InSb substrates using an ion mill. Oxygen was introduced during the milling process to improve the substrates surface quality, and to give better control of the etch selectivity.

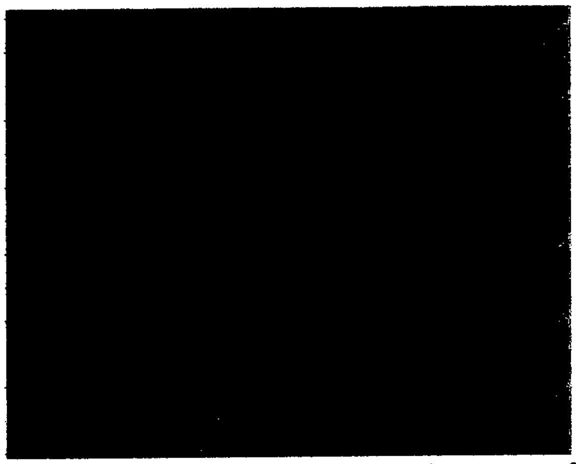

Figure 12. Micrograph of the continuous profile Off-axis field grating lens fabricated in InAs.

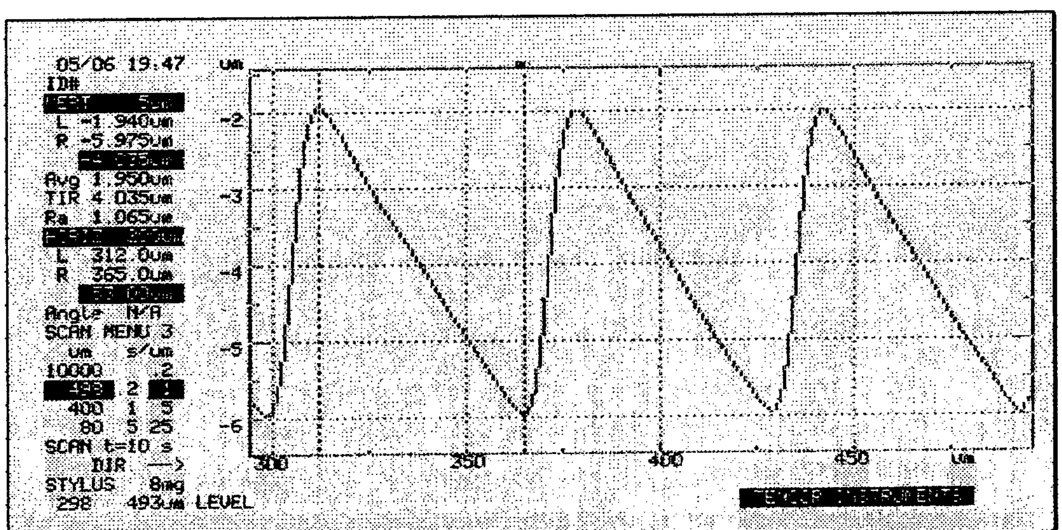

Figure 13. Profilometry scan of the off-axis field grating lens fabricated in InAs, shown in **Figure 12**. Notice the smooth, continuous surface of each of the diffraction zones, and the linearity of the blazed surface. The etch depth of this sample was 4.035 μm. It was etched using an ion mill with gas flow mixtures Ar:54 % and O_2:46 %, yielding a 1.2:1 selectivity.

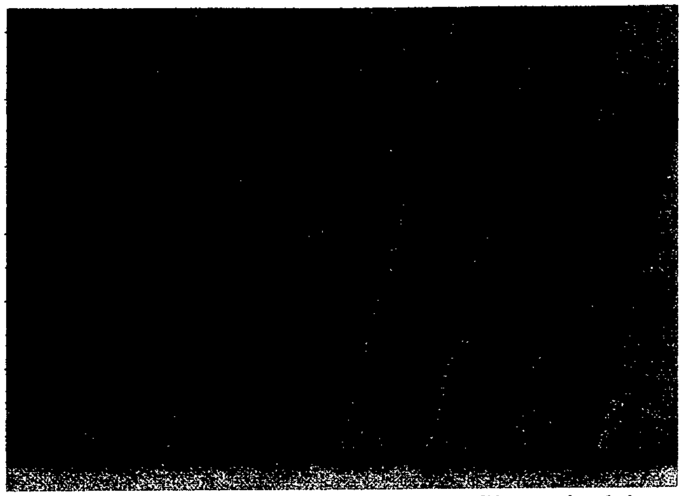

Figure 14. Continuous surface profile etched into InSb during the Phase I contract. This shows only a portion of the off-axis field grating lens fabricated by SY Technology, Inc. during this contract.

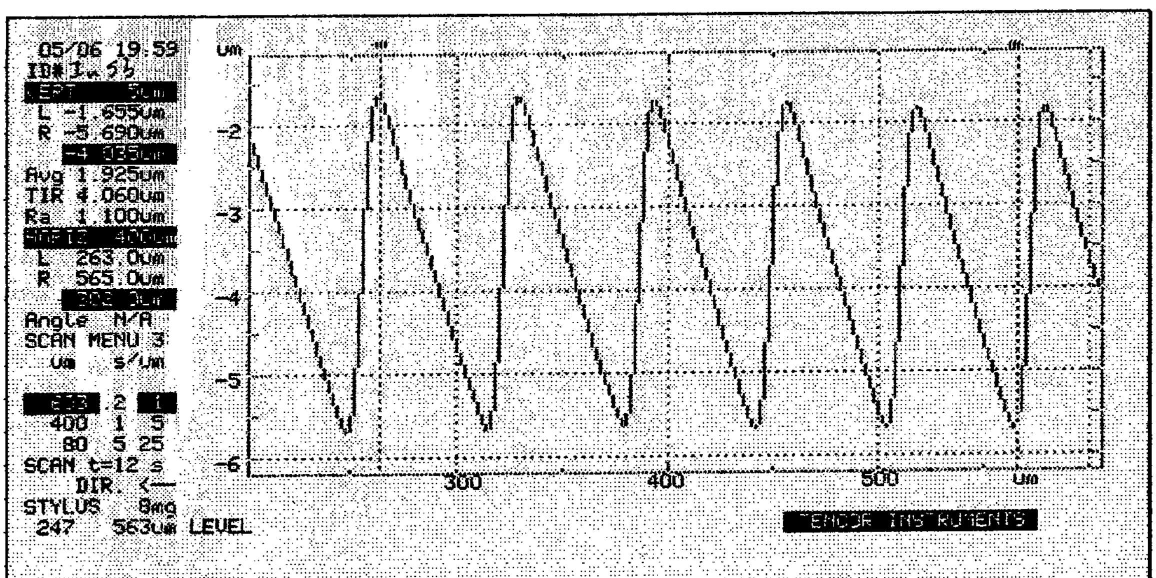

Figure 15. Profilometry scan of the off-axis field grating lens shown in **Figure 14**. Again, notice the linearity of the front blazed surfaces, the uniformity of each of the zones, and the smooth, continuous profile of the surface function.

3. Summary

In this contract, SY Technology, Inc. has demonstrated and answered all of the technical objectives presented in the original proposal. First, we have shown that using MHA reactive ion etching to transfer continuous surface profiles into InSb substrates was not feasible using current production processing methods. This was the first technical objective. Second, we developed a precise photoresist exposure and development process to accurately replicate gray scale mask features. The photoresist which showed the most promise was the Shipley STR 1000 series photoresists. This was the second technical objective. Third, we were able to develop a process to successfully transfer continuous gray scale mask patterns into photoresist, a crucial link in successfully making continuous surface profiles in any material. This was accomplished by means of an ion mill with oxygen. And finally, we were able to successfully etch continuous surface profiles into InAs and InSb. This was the main goal of this SBIR research. As extra effort, beyond the requirements of this contract, we made a continuous gray scale mask of an operational off-axis field grating lens, transferred this pattern into photoresist, and etched the pattern into both InAs and InSb. At the end of this contract, SY Technology, Inc. will deliver not only a final report detailing the results of this research, but will also deliver an off-axis field grating lens in InSb, thus exceeding the goals of this contract. This lens will be used by NVL in field equipment tests.